Inhalation, thermochemical sulphate reduction and processes of ore formation at McArthur River, Northern Territory

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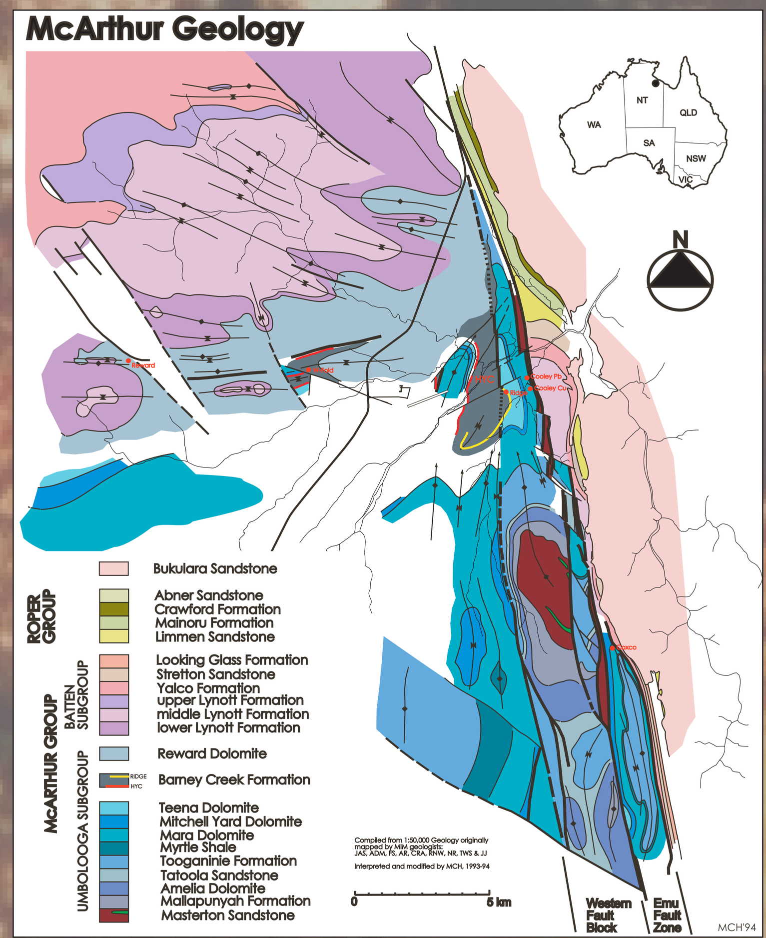
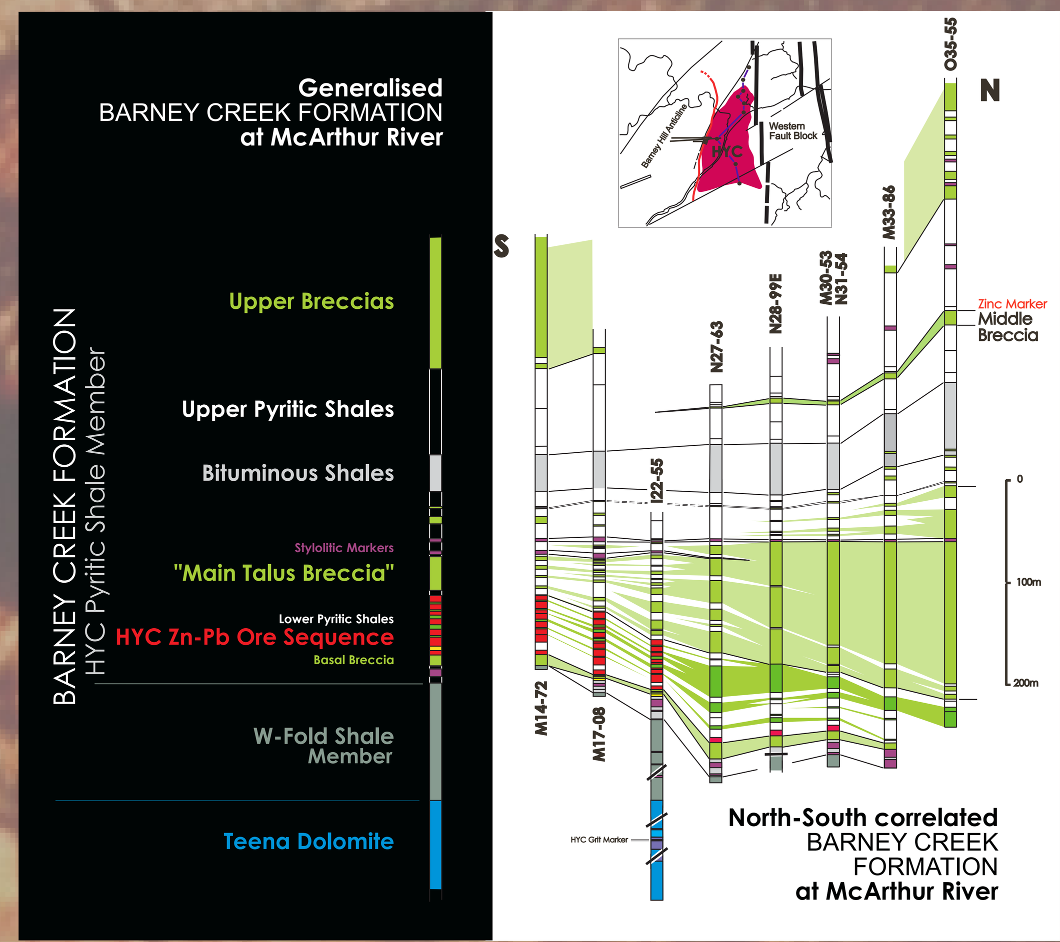
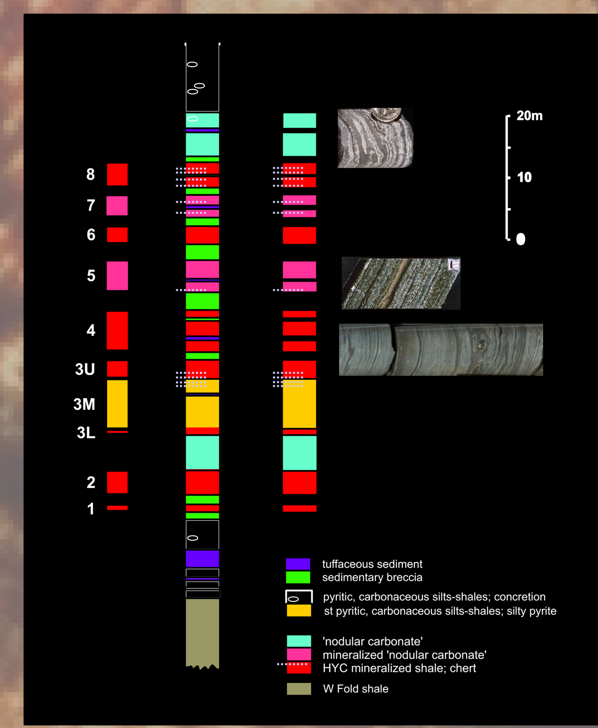
1. INTRODUCTION. The HYC deposit at McArthur River, Northern Territory contains a geological resource of 103.7Mtonnes grading 14.1%Zn, 6.4%Pb and 64g/t Ag that is currently being exploited in an underground room and pillar operation based on a pre-mining, proven and probable reserve of 26.7Mtonnes at14.0%Zn, 6.2%Pb and 63g/t Ag in 2 orebody and 3upper to 4lower orebodies. The deposit is hosted by dolomitic-carbonaceous-pyritic silts and shales of the Palaeoproterozoic Barney Creek Formation - the lowest unit of significant organic accumulation and preservation within the 6km thick, dolomitic-evaporitic McArthur Group.





2. HYC LOCATION. The HYC resource sits on the flank of a large sedimentary breccia fan deposit that is centred to the northeast of the HYC deposit where the thickest sections of Barney Creek Formation accumulated. This is supported by the isopach work of Ross Logan (1979). The distributary fan feeds the Barney basin from the transpressing Emu Fault zone near the Bald Hills-Emu Faults intersection north of HYC. Amazingly, the Barney Creek sedimentary breccias record the progressive exhumation of the entire McArthur Group within the Emu Fault zone within Barney Creek-time. **Individual sedimentary breccia units can be correlated in detail from north of HYC to south of the deposit through the ore sequence, suggesting that no specific depocentre existed at the location of HYC on the fan flank.** Had a depocentre existed it would have been rapidly filled by sedimentary breccias.

3. BARNEY CREEK FORMATION. Away from ore, Barney Creek Formation comprises variable mixtures of three end-member components with contrasting mineralogy and chemistry. The three end-member components are:
'Barney rhythmites' characterised by mm to cm-scale, dolomite detritus, turbidite deposits with signicifant organic content (~3-15%TOC),
'Sedimentary breccias' composed almost exclusively (at the ore sequence level) of recycled dolomitic material and devoid of organics (TOC~0), and
'Tuffaceous sediments' that preserve delicate depositional features frozen in a feldspar-silica mineralogy (TOC~0 also)

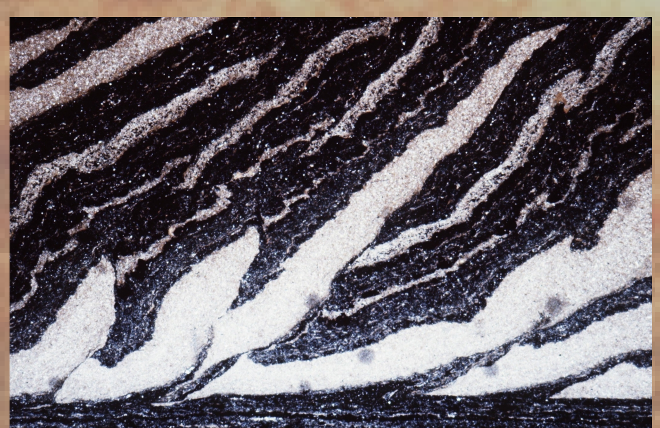


4. ORE SEQUENCE. The HYC ore sequence comprises around 55 meters of 'mineralised shale' arbitrarily divided into 8 orebodies by sedimentary breccia units that essentially dilute the ore sequence. In contrast with the rest of the Barney Creek Formation, the ore sequence is characterised by tuffaceous units with clay mineralogy and an absence of dolomitic concretions. Both these features are thought to reflect the acid conditions of ore formation (*see below*). Three unusual and distinctive lithologies are intimately associated with the ore sequence: 'nodular carbonate', 'mineralised shale' and 'nodular ore' or mineralised 'nodular carbonate'.

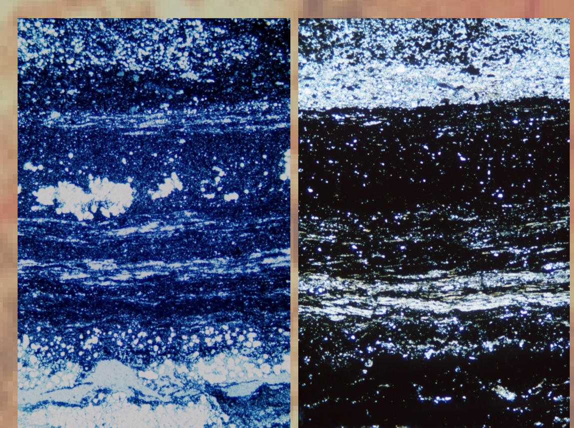
Very specific and significant interactions with, and modifications of, Barney Creek Formation are associated with ore formation. These interactions and modifications suggest that processes of ore formation occur WITHIN the Barney Creek sediment pile, involve significant reaction with the sediment and demand an INHALATIVE, SUB-SEDIMENT-WATER INTERFACE, model for ore formation.

5. SIMPLE COMPARISONS - Ore. Simple hand specimen comparisons of Barney Creek rhythmites outside the ore sequence with ore, demonstrates that ore is NOT simply a product of Barney Creek rhythmite deposition plus 'rained in' sphalerite-galena-(pyrite). One component of the Barney Creek rhythmites is, however, present within ore. The black 'muddy-tops' of the rhythmites are ubiquitously preserved in all samples of 'mineralised shale' as discontinuous, corroded, internally texturally unmodified, muddy detritus (see ultra thin sections). Similarly, nodular carbonate lithologies show good preservation of the 'muddy-top' component of the sediment and the preferential precipitation of the secondary carbonates within the more permeable silty bases of the depositional rhythmites. The apparent bed thicknesses in 'mineralised shale' are at least an order of magnitude finer (<mm scale) than those in the Barney rhythmites outside ore (few mm-cm scale). When all the other components of Barney Crreek Formation are present within the ore sequence, this suggests that significant losses have occurred within the ore sequence.

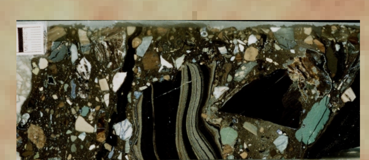
Ubiquitous black muddy-tops in mineralised shale



Ultra thin section of ore imbricate showing white (in transmitted light) 'muddy-tops' comprising equant, texturally-unmodified (aside from marginal corrosion), muddy dolomite detritus and dark wispy 'stylo-laminated' mineralised shale showing weak kinking associated with the imbrication.

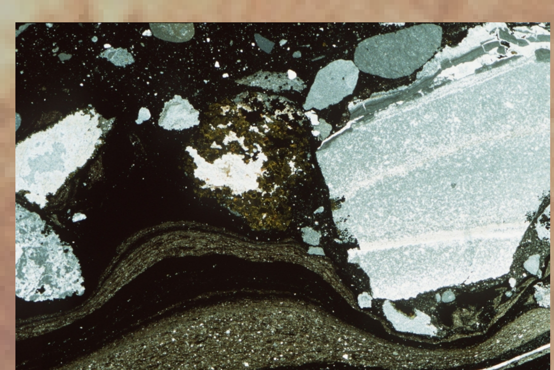


Reflected (R) and transmitted (L) light, ultra thin secions of mineralised shale with a'muddy-top' containing py1 at top and a stylo-laminated sp-gn-py1-py2 sulphide layer through the middle showing that both sulphide and remnant dolomite gangue have wispy, stylo-form.



6. SIMPLE COMPARISONS - Sedimentary Breccias. The sedimentary breccias within the ore sequence contain ample evidence that they were flooded with ore forming fluid. As they are the most permeable units within the sequence this is perhaps not surprising but it does indicate that the ore forming fluid was resident WITHIN the sediment pile. Weak corona sulphide replacement of dolomite clasts and strong sulphide replacement of the minor siliceous clasts within the sedimentary breccias are very common.

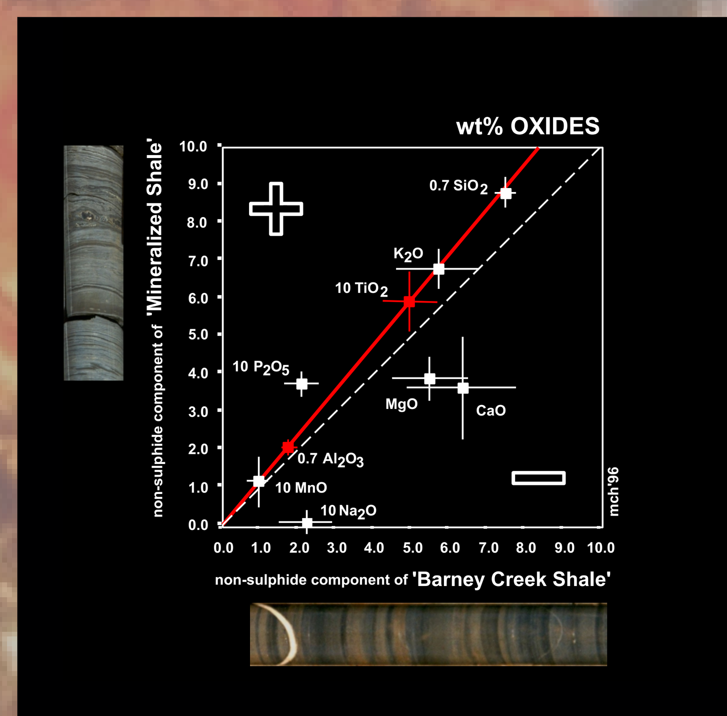
Strong sphalerite replacement of a siliceous clast and weak coronal sulphide replacement of the large dolomitic clasts



7. SIMPLE COMPARISONS - Tuffaceos sediments. The delicate feldspar-silica tuffaceous sediments outside the ore sequence are largely represented by fissile, clayey beds within the ore sequence. In addition, normal diagenetic, dolomitic concretions are ubiquitous outside the ore sequence but are completely absent within it. Both these features reflect the acid conditions generated in the ore-forming environment (see below).

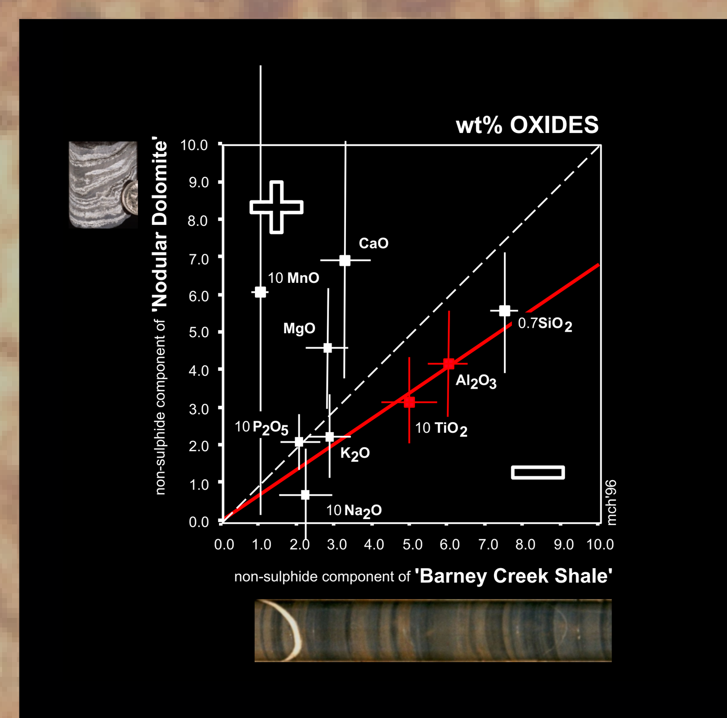
away from ore	in ore
	'clayey muck'
	no concretions

To test whether Barney Creek rhythmites did co-deposit with sulphide 'rain' during ore formation, but have somehow been cunningly disguised in 'mineralised shale', the compositions of the non-sulphide component of ore can be chemically compared with that of background Barney Creek rhthymite.

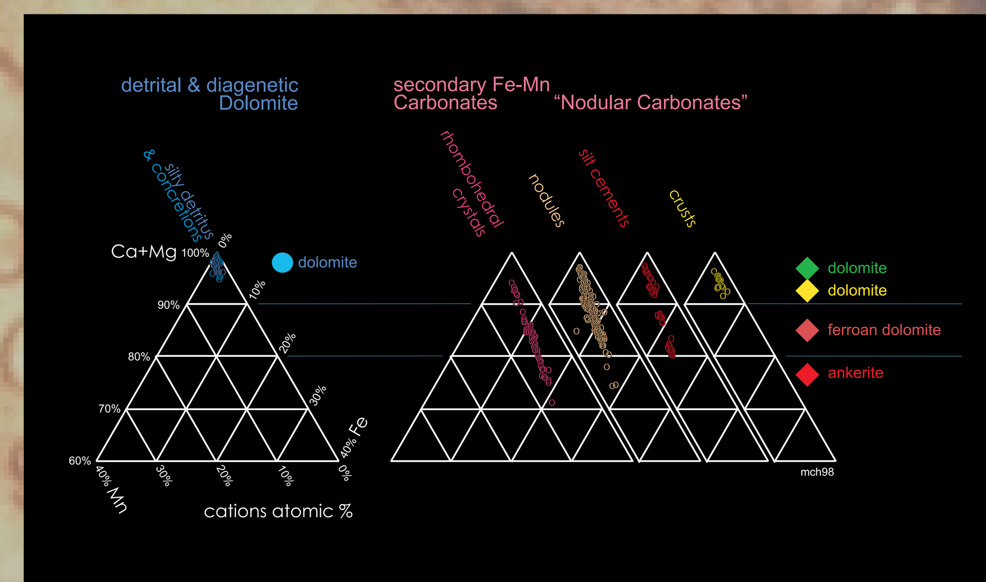


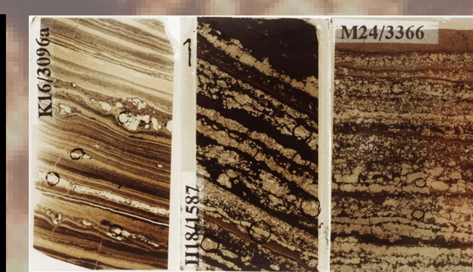
8. CHEMICAL COMPARISONS. Plotting the non-sulphide components of 'mineralised shale' whole rock analyses against those of Barney Creek rhythmite shows that a suite of elements (including some more immobile elements) are relatively CONCENTRATED in 'mineralised shale' and that this concentration is achieved by a relative DEPLETION in Ca and Mg. This suggests that a significant amount of dolomite (calculated to be up to 45% of the original dolomite component of the Barney Creek rhythmite) has been removed in the process of ore formation.

This DOLOMITE LOSS is clearly consistent with the modified apparent bedding thicknesses and the STYLO-LAMINATE texture of ore in ultra thin section and demonstrates very significant SEDIMENT MODIFICATION during ore formation and clear interaction between sediment and an inhaling hydrothermal ore fluid.



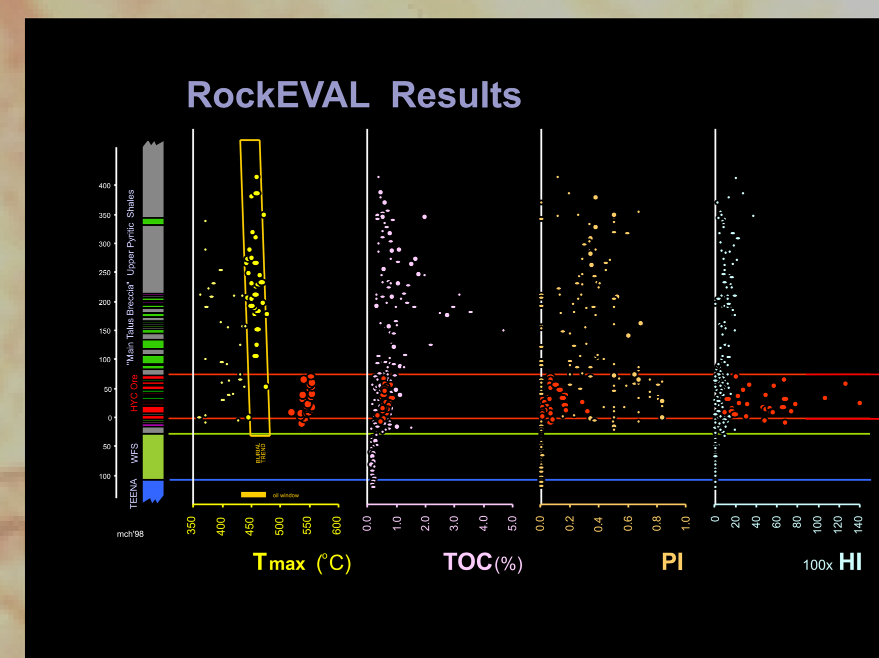
Similarly, plotting the non-sulphide components of 'nodular carbonate lithology' whole rock analyses against those of Barney Creek rhythmite shows that a similar suite of elements are significantly DEPLETED in the 'nodular carbonate lithologies' and that this depletion is achieved by a relative CONCENTRATION in Ca, Mg and Mn. Because Fe can not be successfully divided between sulphide and silicate phases, it falls out of this analysis. However, extensive probe work on the various secondary carbonate components (crystals, nodules, crusts....) associated with the ore system (*see opposite*) shows that they have *manganiferous, ferroan dolomite to ankerite* compositions with constant Mn/Fe = 4.



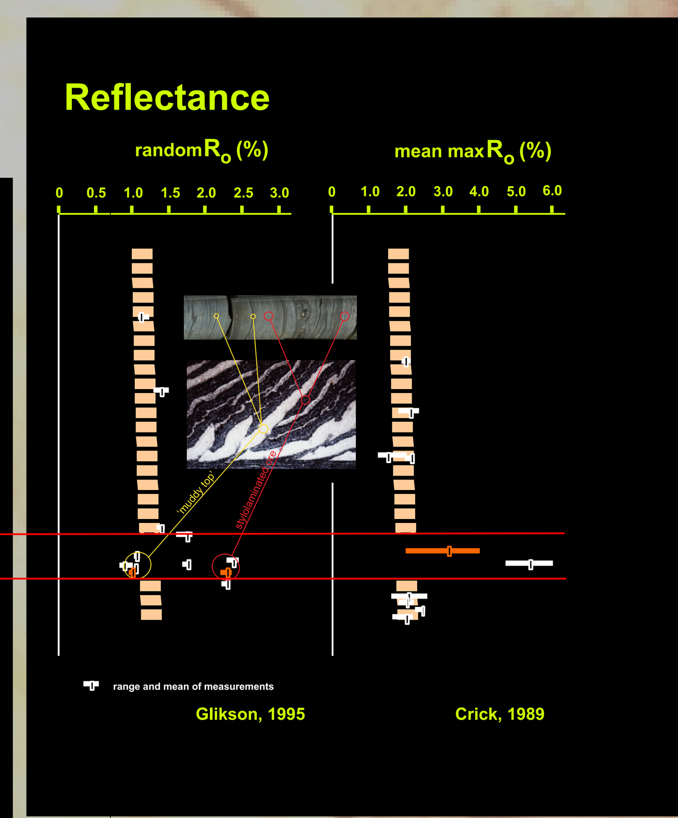


9. CARBONATE CHEMISTRY. Extensive microscope and probe work shows that the 'nodular carbonates, crusts & concretions associated with the ore system form by displacive growth & cementation of porosity, and comprise *manganiferous, ferroan dolomite to ankerite* with constant Fe/Mn = 4.

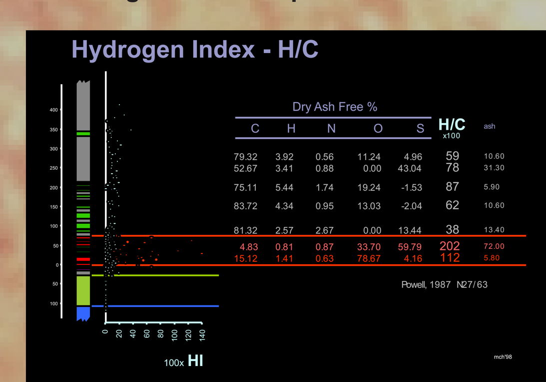
10. ORGANICS. There is an intimate association between high grade, 'mineralised shale' and anomalous organic 'supermaturity'. RockEVAL, reflectance and Dry Ash Free analyses data suggests significant fluid-organic, redox reactions and significant consumption of organic carbon in ore grade 'mineralised shale' samples.



Supermature RockEVAL Tmax's from 'mineralised shale' within the ore sequence (well above the oil window) suggest organic reaction to form intractable organic residues unlike those produced by burial. More importantly, low TOCs within the ore sequence suggest significant organic consumption and, despite having been buried to the top of the oil window, low Production Indices (PI) suggest that the ore zones oil-generative potential was exhausted prior to burial consistent with early redox organic consumption.

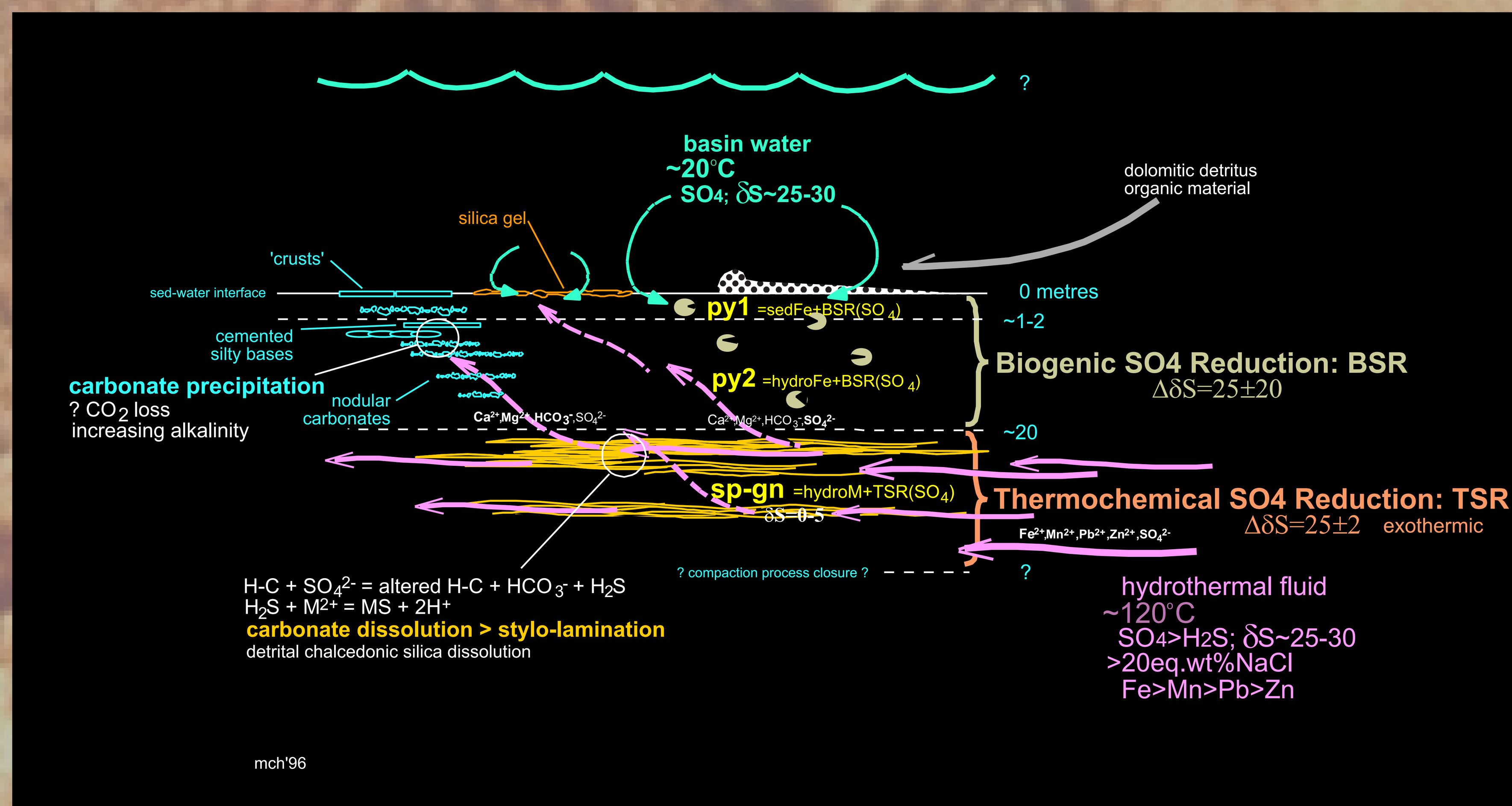


Reflectance measurements parallel the RockEVAL data with 'above-oil window', 'supermaturities' recorded from 'mineralised shale'. **However, very interestingly, reflectances measured within the remnant '*muddy-tops*' within 'mineralised shale' fall back on the burial trend. This observation supports the textural evidence that these muddy portions of the Barney rhythmites are relatively isolated from modification and processes of mineralisation and supports the concept of a strong permeability control on fluid flow and mineralisation process reactions.**



High RockEVAL Hydrogen Indices (HI) within the ore sequence are opposite to burial effects which concentrate C relative to H. High HIs again suggest C consumption relative to H. Dry Ash Free analyses support the RockEVAL HI results.

11. A SUB-SEDIMENT-WATER INTERFACE, INHALATIVE MODEL. An inhalative, sub-sediment-water interface process model rationalises the interactions (major element, isotopic & organic) between host sediment and the ore fluid outlined in this poster. It explains the textural relationships at HYC and is consistent with previously noted 'main game' sulphide paragenetic relationships . It also neatly rationalises the problematic published sulpur data. In this model, base metal mineralization is envisaged to have formed relatively shallowly (~10-20metres) below the sediment-water interface within a laterally-discharging, dense brine that flowed parallel to bedding within the sediment pile. Brine flux was confined to layer-parallel infiltration ('inhalation') of the silty components of the Barney rhythmites (high organics = strong reaction) and the sedimentary breccias (no organics = weak reaction) within the consolidating sediment pile with some component of vertical leakage. This confinement to the coarser, permeable sediments resulted from the more rapid closure of porosity and permeability of the *muddy* portions of the Barney rhythmites on shallow burial (Halley & Schmoker, 1983) and resulted in their ubiquitous textural preservation throughout the otherwise highly texturally modified ore component of the sequence. The dense (up to 20% greater than seawater), low temperature brine had high salinities and sulphate in excess of sulphide ($SO_4 >> H_2S$) and would have been unlikely to have been buoyant. Rather it would have flowed in the available permeability within the sediment pile on *base seals.* A mixing zone between the vertically-leaking, dense brine and the overlying pore/basinal waters would have existed within the accumulating, porous sediment pile and its position would have probably fluctuated within it, occasionally approaching, or even breaching, the sediment-water interface.



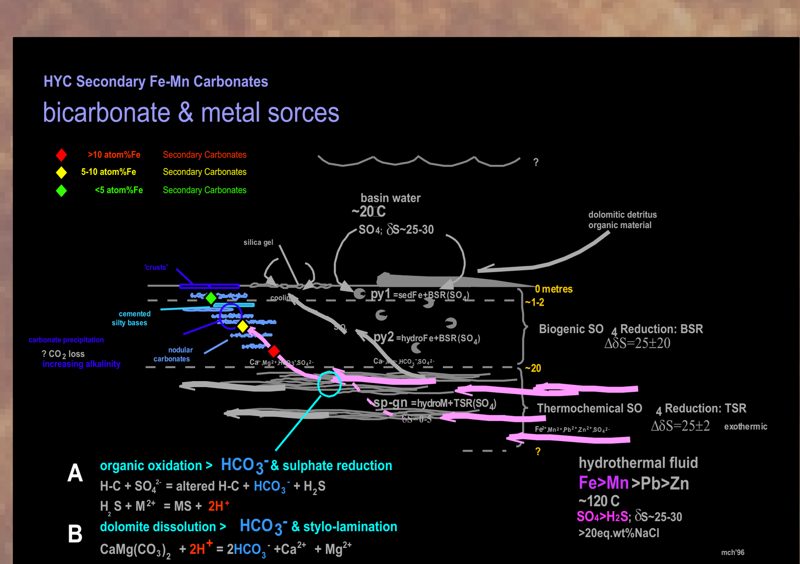
12. INSTANTANEOUS VIEW OF PROCESS. At any instant in time, within the sediment pile, exothermic redox reactions involving the reduction of brine sulphate and the oxidation of organics (thermochemical sulphate reduction provided reduced sulphur for base metal precipitation:

$$H\text{-}C + SO_4^{2-} = \text{altered}H\text{-}C + HCO_3^- + H_2S \qquad (1)\ \text{net reaction}$$

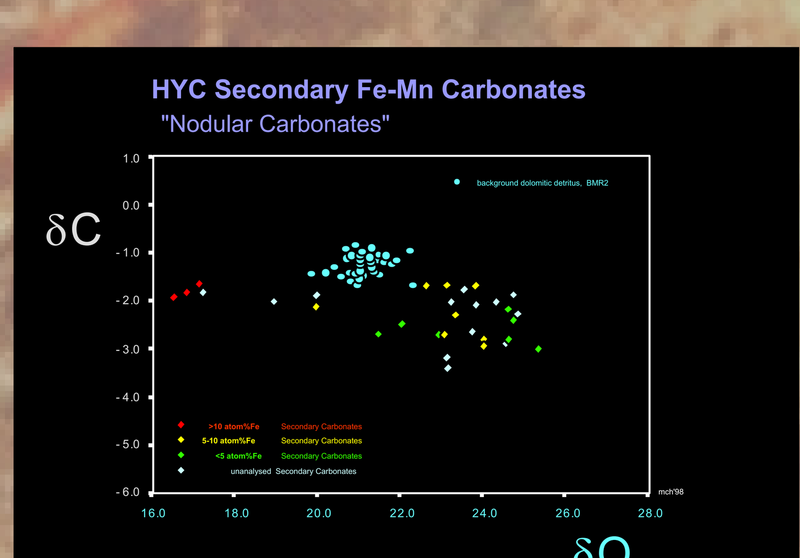
$$M^{2+} + H_2S = MS + 2H^+ \qquad (2)\ \text{sp-gn precipitation}$$

Hydrogen ions, generated in the immediate environment of base metal precipitation (reaction 2) and the production of some organic acid intermediaries during the oxidation of kerogen (reaction1), were neutralised by the dissolution of carbonates to produce the stylo-laminated texture of high grade ore. These processes occurred selectively within the permeable silty bases of the relatively organic-rich, silt-shale rhythmites of Barney Creek Formation. Although the dolomite-rich sedimentary breccias were undoubtedly brine-saturated, the local production of reduced sulphur within them would have been negligible due to their highly diluted organic contents. The local environment of base metal precipitation had a reduced pH as a result of local sulphide precipitation processes which stabilised marcasite and Mn-ankeritic carbonates while destabilising dolomite.

At the same instant in time, above this zone of stylo-dissolution and base metal precipitation, around the sediment-water interface, biogenic processes dominated. Within the first metre or two below the sediment-water interface, pyrite euhedra (sometimes in framboidal clusters; py1) formed from biogenically reduced pore and/or basin sulphate and available sedimentary (plus hydrothermal?) iron - via standard sedimentary-biogenic processes. In the intermediate brine outflow/mixing zone, hydrothermal Fe combined with biogenically-reduced sulphate to form the coarse-grained, overgrowth, hydrothermal pyrite of the HYC sequence; py2. The sulphate consumed within this mixing zone is envisaged to have been a mixture of pore water sulphate and hydrothermal brine sulphate not consumed by base metal sulphide precipitation (*see above*).

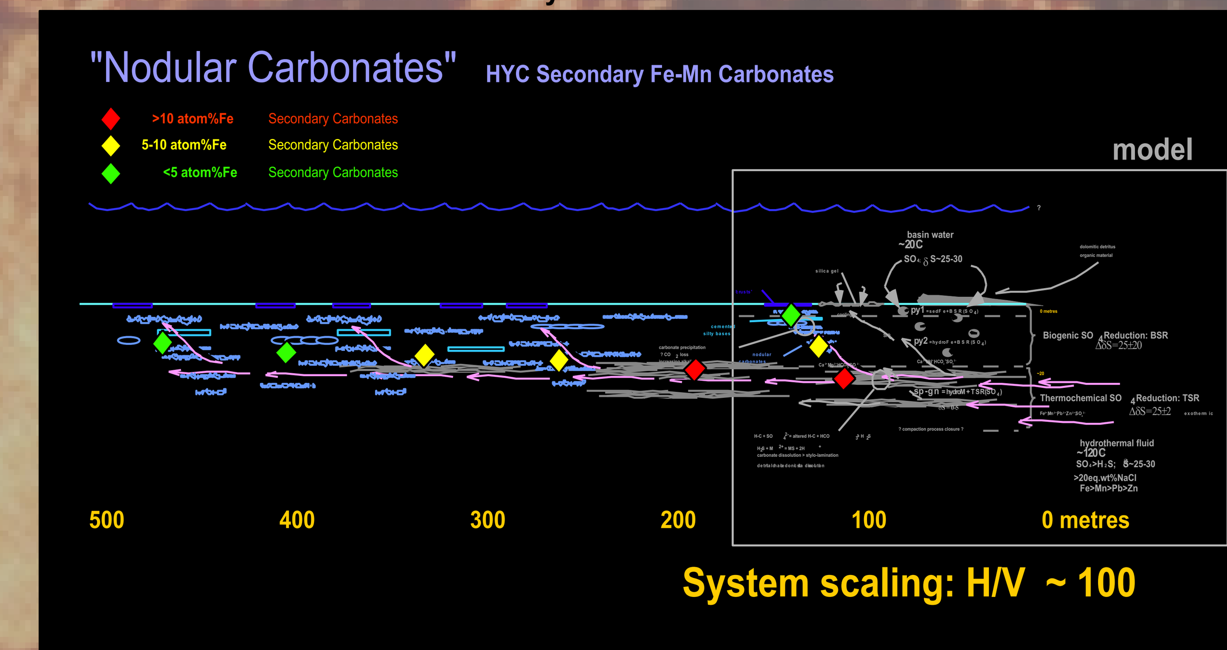


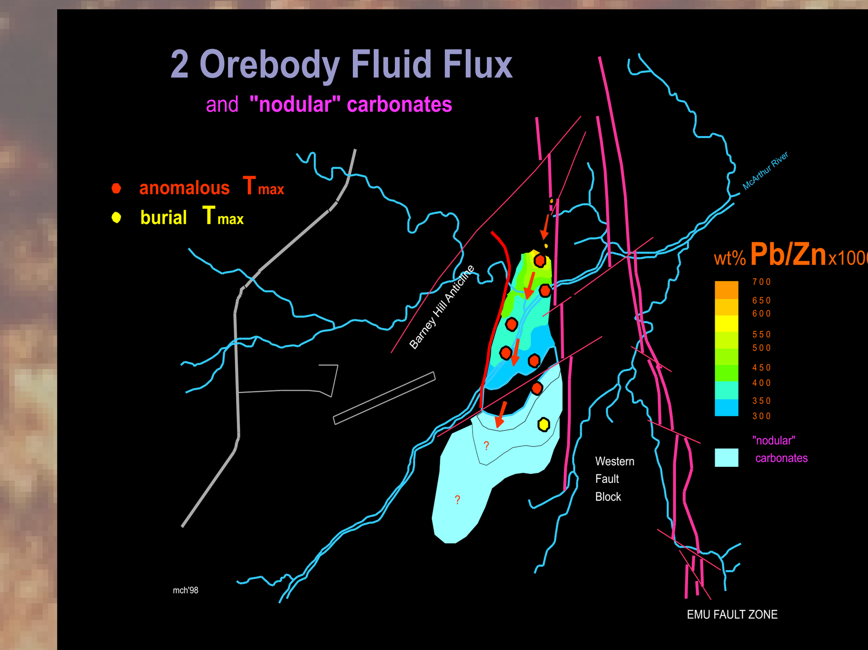
In addition, within this outflow/mixing zone, hydrothermal ferroan dolomitic to ankeritic carbonates precipitated in a variety of 'nodular, crusty and concretionary' habits with constant Fe/Mn ~ 4.0 but generally decreasing absolute (Fe+Mn) component towards the sediment-water interface. Bicarbonate ion is envisaged to have been contributed from carbonate dissolution and organic oxidation (reaction 1) within the base metal zone and the additional cations, Fe and Mn, from the ore-forming brine. Carbonate precipitation within this mixing zone is thought to be in response to increasing alkalinity (pH) and/or CO_2 loss towards the sediment-water interface. Within the base metal zone, the (presumably) quartz-saturated brine also dissolved detrital amorphous silica fragments (commonly replaced by base metal sulphides) and precipitated volumetrically minor quartz euhedra (on initial gentle cooling). Minor silica was dumped: (i) as gel (Oehler & Logan, 1977), on quenching at or close to the sediment-water interface which on subsequent burial recrystallised to black chert (some to be subsequently redissolved by the prograding ore system, see below) and (ii) with Fe, Mn carbonates in distal nodular and cemented zones.



Isotopice work on drilled samples of nodules show a weak light carbon shift (1-3ppt) in the nodules relative to background dolomitic detritus consistent with a light carbon contribution from organic oxidation considerably diluted by a stylo-dissolved, dolomite component derived from the zone of ore formation. Oxygen isotopes show a wide spread from light shifted for higher Fe+Mn, more proximal secondary carbonates to heavy shifted for the lower Fe+Mn, more distal carbonates carbonates.

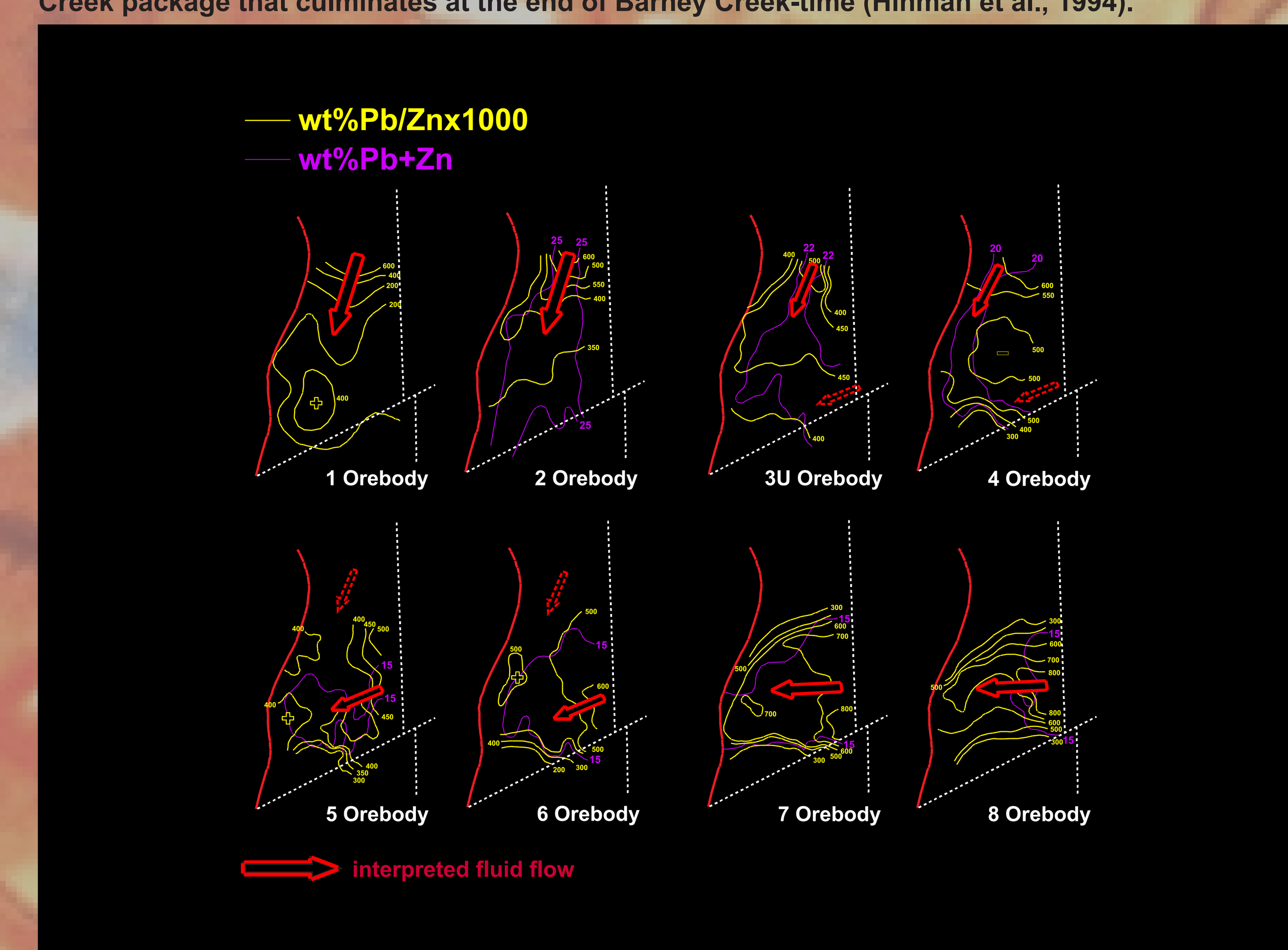
13. ORE SEQUENCE AGGREGATION. The ore sequence is envisaged to have built by vertical aggregation of sediment with the accompanying upward-stepping and successive overprinting of py1-py2-base metal zones and carbonate & silica precipitation and dissolution zones. This process accounts for the well-documented sulphide paragenetic relationships (Williams, 1978; Eldridge et al., 1993) and the ubiquitous textural modification of (py1-)py2, 'nodular, crusty and concretionary carbonates' and chert by intense stylo-lamination in high grade ore. It should be emphasised that as the dominant flux of brine is parallel to the sediment permeability (horizontal), the instantaneous zonations of basemetal sulphide-py2-py1, carbonate dissolution and precipitation and silica dissolution and precipitation are skewed hugely parallel to bedding. Therefore, the 'instantaneous', ten metre vertical zonation outlined above also describes a zonation pattern parallel to bedding in the 'downstream' brine direction at a 'many hundreds of metres' scale.



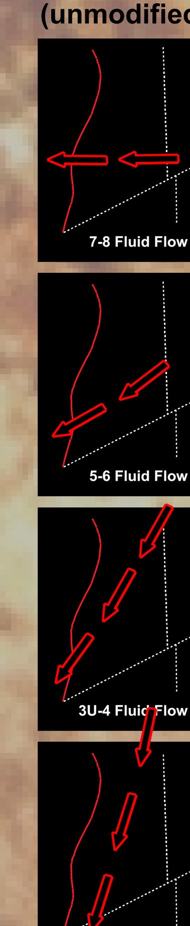


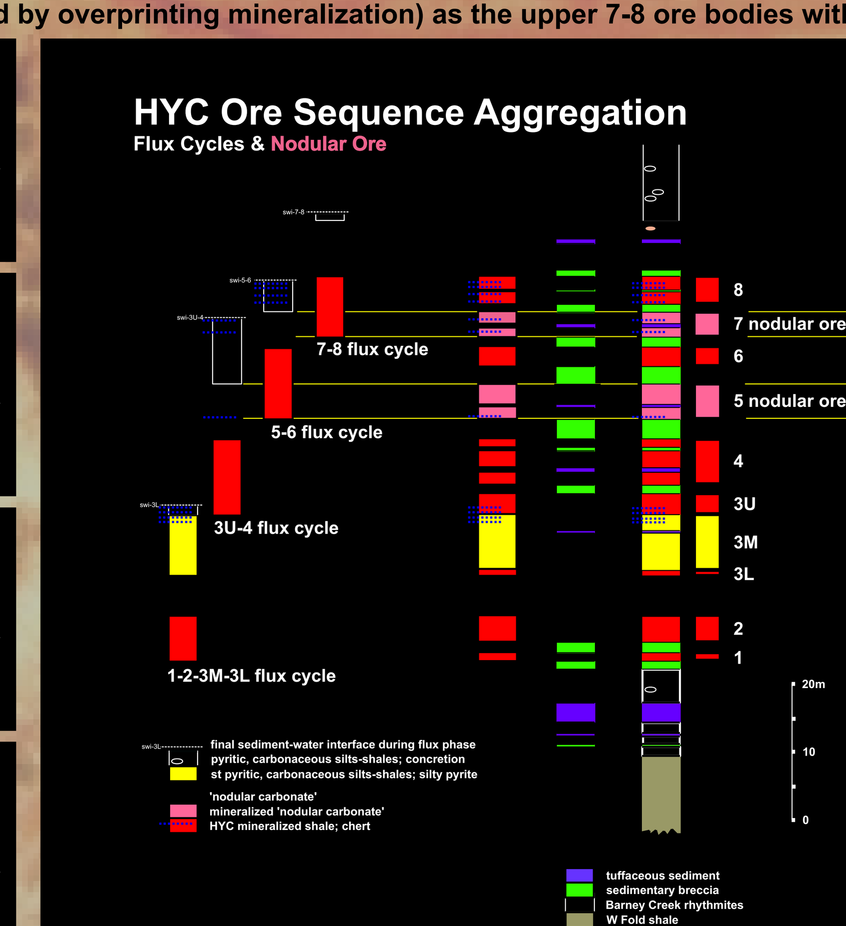
The nodular zone is well developed within the outflow zones of 1 and 2 orebody. The current resource is centred over high grade 2 orebody which overlies the nodular outflow zone of 1 'orebody'. A 1 orebody sulphide zone is intersected in deep holes to the north of the HYC resource.

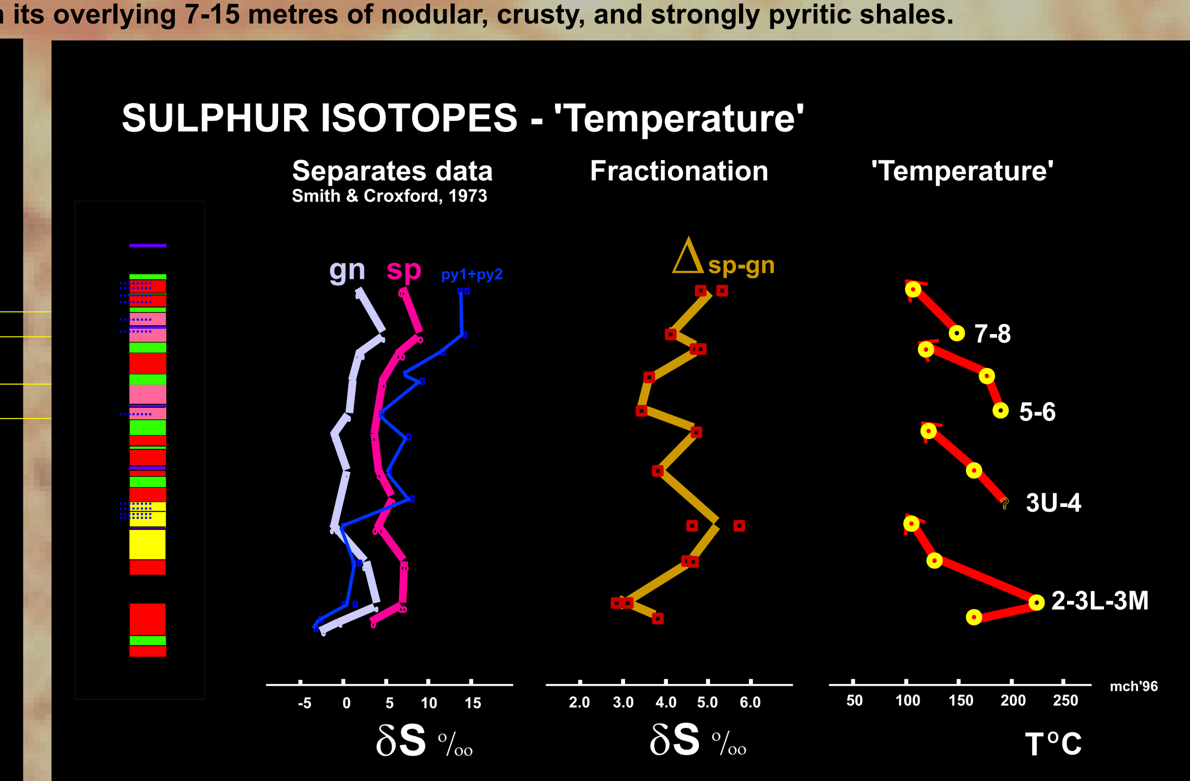
14. SHIFTING BRINE FLUX. The metal distribution patterns (previously Logan, 1979) suggest that during the vertical aggregation of the HYC ore sequence, there were four distinguishable phases of relatively shifted brine flux. Each phase would have approximated two presently defined orebodies and represented a period of steady state fluid flow through the recently deposited and accumulating sediments. Each phase was clearly separated from the subsequent phase by some rearrangement within the plumbing system but also by significant modifications in the basin floor topography that shifted the position of the within-sediment brine flux. This is reflected in progressive shifts in the locus of maximum total metal grade up through the ore sequence that are consistent with transpressive deformation of the accumulating Barney Creek package that culminates at the end of Barney Creek-time (Hinman et al., 1994).



15. CYCLE STACKING.. Apart from the spatial metal distribution patterns, memory of the four fluid flux phases is preserved by virtue of the cyclic vertical distribution of high grade mineralization, 'nodular, concretionary and crusty carbonates' and strong pyrite (py2) through the ore sequence. The final flux phase is preserved (unmodified by overprinting mineralization) as the upper 7-8 ore bodies with its overlying 7-15 metres of nodular, crusty, and strongly pyritic shales.

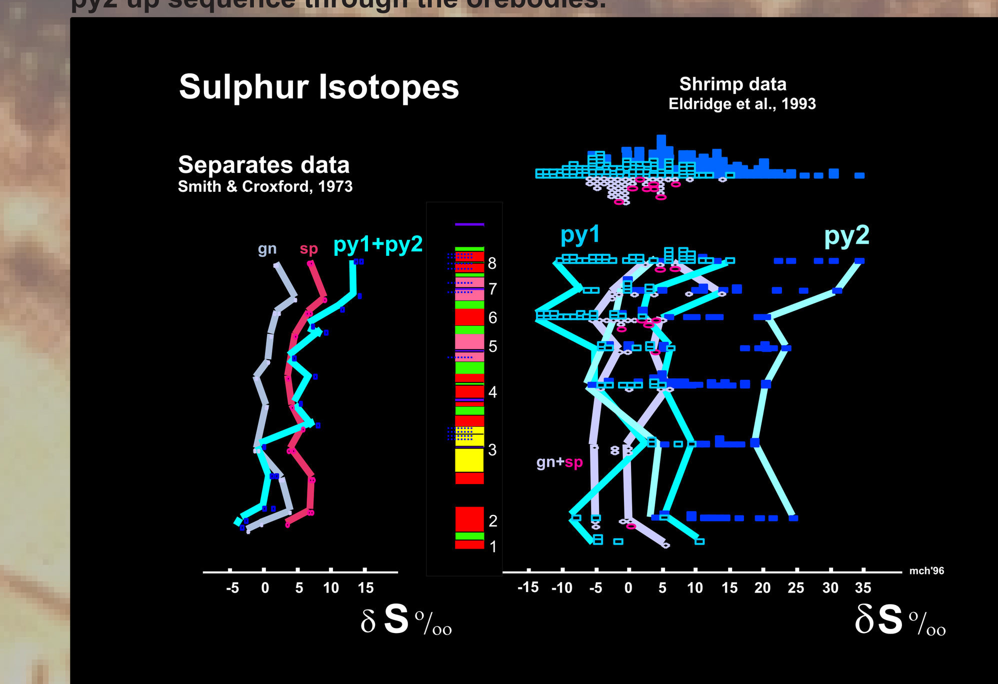






In addition, the sphalerite-galena fractionation temperatures derived from a cavalier treatment of Smith & Croxford's single profile separates data, also reveals four distinctive temperature cycles that exactly match those suggested by the switches in the metal ratios in plan view.

16. SULPHUR ISOTOPE SYSTEMATICS. The SHRIMP delta^{34}S data of Eldridge et al. (1993) and the sulphide-separate delta ^{34}S data of Smith and Croxford (1973) together provide a one-dimensional view of the sulphur isotopic variation of sulphides (py1-py2-sp-gn) within the ore sequence at HYC. Both py1 and py2 have biogenic isotopic spreads with py2 showing a heavy shift up sequence. The sulphur isotopic spread of py1 is consistent with *moderate* biogenic fractionations (delta^{34}S=25-15; due to relatively low kinetic isotope effects (Ohmoto, 1986; Ohmoto & Rye, 1979), driven by high sedimentation rates, high nutrient levels and high rates of sulphate reduction) from Proterozoic waters with sulphate delta^{34}S=25-30 (Berner,1989; Holland, 1992; Grotzinger & Kasting, 1993; Logan et al., 1995). A similar py1 distribution exists throughout the Barney Creek Formation outside the ore sequence and represents background biogenic pyrite formation. Pyrite2 is a distinctive associate of the ore system. The heavy shift in py2 up-sequence is not satisfactorily explained by closed system (with respect to sulphate) behaviour (Eldgridge et al., 1993) because of the problem of py2's ubiquitous co-existance with open system biogenic py1. Open and closed systems can not coexist in a biogenic sulphate reduction zone at the same time. In the model presented here, py2 forms in the "instantaneous' view, within an intermediate depth zone between biogenic py1 and thermochemical base metal sulphide precipitation, by dominantly biogenic processes but from residual brine sulphate not consumed within the base metal zone. This outflow sulphate would have been heavy-shifted by the precipitation of stratiform base metal sulphides with delta ^{34}S=0-5 (Eldridge et al., 1993; Smith & Croxford , 1973) relative to the primary brine supply whose sulphate had delta^{34}S=30 (based on sulphates precipitated with base metal sulphides within the Cooley Breccias from refocussed brine flow at the end of Barney Creek-time; Hinman, 1995). A decrease in the absolute amount of sulphate in the hydrothermal brine or its relatively more complete thermochemical reduction to form stratiform base metal sulphides with time would account for the increasingly heavy shift in py2 up sequence through the orebodies.



17. CONCLUSIONS. There is ample textural, paragenetic, chemical, isotopic and organic evidence of significant sediment-hydrothermal fluid interaction associated with ore formation at HYC McArthur River.

- The Barney rhythmite component of the host succession is apparently absent or highly modified (as argued here) within the ore sequence while the other end member components (sedimentary breccias and tuffs) are identifiable in variously altered states within the ore sequence and outside it..
- Mineralised shale is characterised by stylo-laminated sulphide layers and texturally unmodified *muddy-tops* suggesting that permeability-controlled dissolution process are directly linked to ore formation
- Stylo-lamination is explained by a very significant dolomite loss from the original Barney rhythmite component that is the ultimate host of ore
- Texturally all mineralisation overprints 'diagenetic' features that are accepted as forming within the sediment pile both within the ore sequence and outside it. **Mineralisation must, therefore, also form within the sediment pile.** These pre-ore components include biogenic py1, biogenic py2, the 'nodular carbonates' and chert
- Significant C organic deficits and anomalous organic geochemisrty associated with the ore zone, in comparison with the rest of the host sequence, suggests the consumption of the water-lain organics within the sediment pile in organic-sulphate redox reactions ...... thermochemical sulphate reduction
- A model that rationalises: the clear presence of hydrothermal fluid within the sediment pile, the significant whole rock, isotopic and organic modifications of the permeable, organic-rich components of the host succession, the clear permeability-control on some textural and organic modification , and the co-existance of an open, biogenic py1 system with a closed, biogenic py2 system is the **sub-sediment water interface, inhalative model** presented here.
- A **sub-sediment water interface, inhalative model** does not require the unrealistic maintenance of a tidily, Pb/Zn-zoned, brine pool perched on the flank of an active turbidite fan system with regular mass flow deposition crossing the whole region of ore formation. Clearly ore formation in the sub surface is unaffected by surface turbidite deposition and can produce smoothly metal-zoned ore sequences from the prograding flux of hydrothermal fluid within the available permeability of the host succession.

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